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THE PARACHOR AND THE P → O BOND

Richard G. Gillis and R. Ian Tilley

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ABSTRACT

The bond parachors *P* (P - O) and *P* (P → O) have been determined as 21.4 and 17.3 respectively. This result supports the contention that the *(P → O) bond in phosphates, phosphonates etc., is a two-electron* dative bond and not a four-electron bond.

The bond parachors *P* (P - H), *P* (P - C), and *P* (P - Cl) have also been determined.

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16. *ABSTRACT (if this is security classified, the announcement of this report will be similarly classified):*

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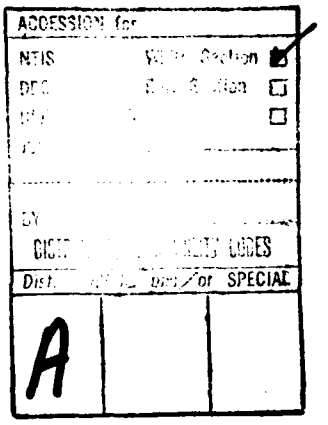


THE PARACHOR AND THE P → O BOND

INTRODUCTION

The P → O bond refraction was intensively studied in these laboratories some years ago (1) because of its relevance to the structure and mechanism of action of phosphorus-containing CW agents. Recently an apparatus for the determination of surface tension was constructed (2). The opportunity has been taken to examine the parachor of bonds to phosphorus, particularly P → O.

The parachor is defined by the relation

$$[P] = \frac{M \quad \gamma^{\frac{1}{4}}}{D - d}$$

where M is the molecular weight, γ is the surface tension, D is the density of the compound as liquid, d is the density of the compound as vapour. The only constraint is that γ, D and d should be determined at the same temperature. The density of the vapour can be neglected except in determinations near the boiling point of the liquid. The parachor is a constitutive property of covalent molecules i.e. it is one which can be divided into contributions by particular atoms, by different kinds of bonds between atoms, or by specific structures or sub-structures. The contributions (usually additive) can be combined to give a predicted value of the property for a compound as yet unprepared, to distinguish between possible structures of a compound, or to provide an estimate of the consistency of the reported physical properties of a compound.

The parachor is a measure of the molecular volume at standard internal pressure. It was studied extensively by Sugden during the period 1920-1930 (3). A relevant example of its use was by Mumford and Phillips, who showed that the product of the further chlorination of mustard gas (2,2'-dichlorodiethyl sulphide) was a derivative of ethyl vinyl sulphide, HCl having been eliminated during the chlorination (4).

Sugden's treatment of his experimental results assigned positive values to individual atoms and zero to the contribution of normal single covalent bonds. Double and triple covalencies and rings had large positive values. Sugden's arithmetical methods are open to criticism. Vogel (5) who made extensive parachor and bond refraction measurements somewhat later (1940-1950)

used an acceptable least squares method for data handling, which had been developed by Vickery and Denbigh for bond refractions (6). Vogel's treatment assigns zero values to atoms, and positive values to single covalencies. A partial listing of Vogel's bond parachors is given in Table 1.

Molecular refraction is another constitutive property of covalent molecules; it is defined by the relation

$$[R]_D = \frac{M}{\rho} \frac{n^2 - 1}{n^2 + 2}$$

where M is the molecular weight, ρ is the liquid density, n is the refractive index for the sodium D- line. Both ρ and n should be determined at the same temperature and most work has been standardized at 20 or 25°C. The molecular refraction can be divided into contributions by different kinds of bonds (atoms are considered to give zero contribution). Some bond refractions are given in Table 2. It can be seen that dative covalencies have negative or small positive bond refractions.

TREATMENT OF DATA

Molecular parachor determinations have been made on four trialkyl phosphites (Table 3), four dialkyl phosphonates (Table 4), and three dialkyl alkylphosphonates (Table 5). Literature values for four trialkyl phosphates are given in Table 6. The bond parachor P (P → O) was determined by direct subtraction: P (alkyl phosphate) - P (alkyl phosphite). Using this value of P (P → O) and Vogel's values for P (C - H), P (C - C) and P (C - O) for acetals (Table 1), P (P - O) was calculated from P (alkyl phosphite). Using these values, P (C - P) was then calculated from P (dialkyl alkylphosphonate) and P (P - H) from P (dialkyl phosphonate). The results are included in Table 1.

Other relevant bond parachors were determined from available literature values. The bond parachor P (P - Cl) was derived directly from the molecular parachor P (PCl_3). Two values of P (PCl_3) have been reported 199.0 (7) and 201.1 (8). Taking one-third of the mean gives P (P - Cl) 66.6. Two values of P ($POCl_3$) have also been reported, 217.6 (8) and 217.6 (9). From P ($POCl_3$) - P (PCl_3) we have P (P → O) 17.6, agreeing with the value from esters (17.3). From the data of Ramsay and Shields (8), P (S_2Cl_2) is 205.1. Using P (S - S) = 49.0 (3), we have P (S - Cl) = 78.1. For making comparisons, these values are also listed in Table 1.

DISCUSSION

The Phosphorus-Oxygen Bond Parachor

It has been argued (1,10) that the negative or small positive values of R (P → O), as shown in Table 2, support the formulation of the phosphorus-oxygen bond in phosphates, phosphonates, etc., as a dative two-electron bond rather than a normal covalent double (four-electron) bond.

The bond parachors now reported in Table 1 also support this conclusion. The (P → O) bond parachor is slightly less than P (P - O) and has the same magnitude as P (S → O) and P (N → O) which are respectively much less than and slightly greater than P (S - O) and P (N - O). In contrast, parachors of undisputed double (four-electron) bonds are greater than those of the corresponding single bonds by a factor of about 3 to 7; those of triple (six-electron) bonds are greater still by a further factor of about 2.

Because there is no theoretical or empirical relation between bond parachors and bond refractions, the parallelism of their magnitudes gives more credence to the conclusion than if either property is considered separately.

Parachors of Other Bonds to Phosphorus

The bond parachor P (P - C) is smaller than was expected but it is concordant with the values for other single bonds to carbon. The same general statement can be made about both P (P - H) and P (P - Cl).

EXPERIMENTAL

Materials

As far as possible compounds studied were available off the shelf either as commercial samples, or laboratory specimens prepared for other purposes. The following commercial samples were used without further purification: triethyl phosphite (Aldrich), diethyl phosphonate (Aldrich), di-*n*-propyl phosphonate (Eastman), di-*iso*-propyl phosphonate (Aldrich) and di-*n*-butyl phosphonate (Aldrich). The following laboratory specimens were used without further purification: tri-*n*-butyl phosphite, diethyl ethylphosphonate, diethyl allylphosphonate and di-*n*-propyl *n*-propylphosphonate.

Tri-*iso*-propyl phosphite was purified by refluxing over sodium and fractionation under reduced pressure. Tri-*n*-propyl phosphite was prepared by standard methods (11) and purified by distillation over sodium.

An estimate of the purity of each compound was made by gas chromatography.

Physical Measurements

Density measurements were made using a Sprengel pycnometer as modified by Hennion (12).

Surface tension measurements were made using the maximum bubble pressure method (2). Measurement of the difference in maximum pressure, P, required to liberate bubbles from two glass tubes, one of small diameter and the other of capillary size, immersed in the liquid of interest enabled the surface tension of the liquid to be determined using equation 1 (13).

$$\gamma = \left(AP \quad 1 + 0.69r \frac{gD}{P} \right) \tag{1}$$

where, γ (dyne cm^{-1}) = surface tension of the liquid,

P (dyne cm^{-2}) = pressure difference (see text),

g (cm sec^{-2}) = acceleration due to gravity,

D (g cm^{-3}) = density of the liquid,

A = an apparatus constant,

r (cm) = radius of the larger tube.

In the apparatus used in this work, A was found to be 0.01021 by calibration with purified benzene and water (2) and r = 0.1983 cm. Pressures were measured using a toluene-filled manometer.

Note on Units Employed

Sugden and Vogel both worked in c.g.s. units; for this reason, these units have been retained so that our parachor units are the same as Vogel's. Surface tension which used to be quoted in dyne cm^{-1} (and was numerically the same as surface energy in ergs cm^{-2}) in S.I. units is Newton m^{-1}. The numerical relation is :

$$1 \text{ N } m^{-1} = 10^3 \text{ dyne } cm^{-1}$$

or

$$1 \text{ mN } m^{-1} = 1 \text{ dyne } cm^{-1}$$

REFERENCES

1. Gillis, R.G., Horwood, J.F. and White, G.L. (1958). *J. Amer. Chem. Soc.*, 80, 2999.

2. Gillis, R.G. and Tilley, R.I. (1979). (In preparation).

3. Sugden, S. (1930). "*The Parachor and Valency*", George Routledge and Sons Ltd., London, and references therein.

4. Mumford, S.A. and Phillips, J.W.C. (1928). *J. Chem. Soc.*, 155.

5. Vogel, A.I., Cresswell, W.T., Jeffrey, G.H. and Leicester, J. (1952). *J. Chem. Soc.*, 514 summarizes the earlier papers.

6. Vickery, B.C. and Denbigh, K.G. (1949). *Trans. Faraday Soc.*, 45, 61.

7. Morgan, J.L.R. and Daghlian, G.K. (1911). *J. Amer. Chem. Soc.*, 33, 672.

8. Ramsay, W. and Shields, J. (1893). *J. Chem. Soc.*, 63, 1089.

9. Freeman, A. and Sugden, S. (1928). *J. Chem. Soc.*, 263.

10. Gillis, R.G. (1960). *Rev. Pure and App. Chem. (Aust.)*, 10, 21.

11. Ford-Moore, A.H. and Perry, B.J. (1963). "*Organic Synthesis*", Coll. Vol.IV, p.955. New York: Wiley.

12. Hennion, G.F. (1937). *Ind. Eng. Chem., Anal. Ed.*, 9, 479.

13. Harkins, W.D. (1949). "*Technique of Organic Chemistry*", (ed. A. Weissberger), Vol.I, Part I, Chap.X. New York: Interscience Publishers Inc.

14. Vogel, A.I. and Cowan, D.M. (1943). *J. Chem. Soc.*, 16.

TABLE 1

PARACHORS OF SOME COVALENT AND DATIVE BONDS*

Atoms Bound	P (E - E′)	P (E = E′)	P (E ≡ E′)	P (E → O)
C...C	4.3	28.5	53.5	
C...N	6.4	29.3	61.4	
C...O	11.3	40.3		
C...P	4.4†			
C...S	26.6	70.9		
N...N	6.2	44.8		
N...O	14.1	52.2		17.6
S...O	34.8			17.8
P...O	21.4			17.3
C...H	17.85			
N...H	19.9			
O...H	20.3			
S...H	42.1			
P...H	27.7			
C...Cl	57.4			
S...Cl	78.1			
P...Cl	66.1			

* Ref. (5), Table 1, p.531.

† Underlined values were obtained in this work.

TABLE 2

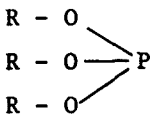
REFRACTIONS OF SOME COVALENT AND DATIVE BONDS*

Atoms Bound	R (E - E′)	R (E = E′)	R (E ≡ E′)	R (E → E′)
C...C	1.296	4.17	5.87	
C...N	1.57	3.76	4.82	
C...O	1.46	3.49		
C...S	4.61	11.91		
N...N	1.99	4.12		
N...O	2.43	4.00		+ 1.78
P...O	3.18			- 1.22
P...S	6.6			6.4
S...O	4.94			- 0.20 esters
				+ 0.60 sulphoxides
				+ 0.40 sulphones

* Ref. (10), Table 5, p.29.

TABLE 3

EXPERIMENTAL MOLECULAR PARACHORS - TRIALKYL PHOSPHITES



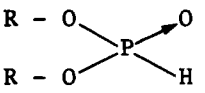
Compound	Purity* (%)	T°C	Density (g cm^{-3})	Surface Tension (dyne cm^{-1})	Parachor
Triethyl phosphite	95	20.0	0.9588	23.40	383.6
		30.0	0.9483	22.88	383.2
		40.0	0.9376	22.09	384.2
					383.6†
Tri-*n*-propyl phosphite	98	20.0	0.9313	24.93	499.6
		30.0	0.9220	24.26	501.3
		40.0	0.9128	23.29	501.2
					500.6
Tri-*iso*-propyl phosphite	98	20.0	0.9043	21.18	494.0
		30.0	0.8950	20.42	494.6
		40.0	0.8851	19.67	495.5
					494.7
Tri-*n*-butyl phosphite	97	20.0	0.9137	23.87	605.6
		30.0	0.9049	23.25	607.5
		40.0	0.8963	22.63	609.1
					607.0

* Found by gas chromatography.

† Mean values.

TABLE 4

EXPERIMENTAL MOLECULAR PARACHORS - DIALKYL PHOSPHONATES



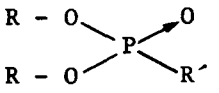
Compound	Purity* (%)	T°	Density (g cm^{-3})	Surface Tension (dyne cm^{-1})	Parachor
Diethyl phosphonate	> 98	20.0	1.0730	29.92	301.0
		30.0	1.0627	28.78	301.0
		40.0	1.0524	28.14	302.2
					301.4†
Di-*n*-propyl phosphonate	98	20.0	1.0196	28.80	377.5
		30.0	1.0101	27.69	377.3
		40.0	1.0006	26.76	377.7
					377.5
Di-*iso*-propyl phosphonate	> 97	20.0	0.9977	25.77	375.2
		30.0	0.9880	24.63	374.7
		40.0	0.9787	23.76	374.8
					374.9
Di-*n*-butyl phosphonate	94	20.0	0.9875	27.85	451.8
		30.0	0.9785	26.28	449.4
		40.0	0.9698	25.48	449.9
					450.4

* Found by gas chromatography.

† Mean values.

TABLE 5

EXPERIMENTAL MOLECULAR PARACHORS - DIALKYL ALKYLPHOSPHONATES



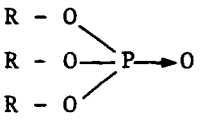
Compound	Purity* (%)	T°	Density (g cm^{-3})	Surface Tension (dyne cm^{-1})	Parachor
Diethyl ethylphosphonate	97	20.0	1.0306	26.65	366.3
		30.0	1.0209	25.34	365.2
		40.0	1.0112	25.09	367.8
					366.4†
Diethyl allylphosphonate	92	20.0	1.0371	28.96	398.5
		30.0	1.0274	27.06	395.5
		40.0	1.0178	26.46	397.0
					397.0
Di-*n*-propyl *n*-propylphosphonate	88	20.0	0.9785	27.36	486.6
		30.0	0.9695	26.37	486.7
		40.0	0.9609	25.22	485.6
					486.3

* Found by gas chromatography.

† Mean values.

TABLE 6

RECORDED MOLECULAR PARACHORS - TRIALKYL PHOSPHATES*



Compound	Parachor
Triethyl phosphate	399.9
Tri-*n*-propyl phosphate	515.9
Tri-*iso*-propyl phosphate	509.9
Tri-*n*-butyl phosphate	629.2

* Ref. (14)

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